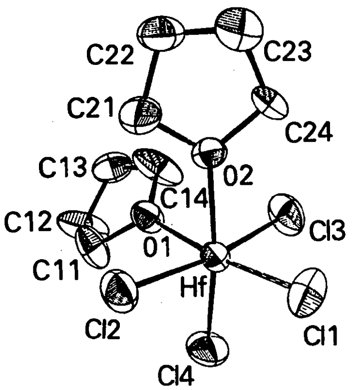

Fig. 1. *ORTEP* (Johnson, 1976) drawing of the [*cis*-$HfCl_4(THF)_2$] molecule. Thermal ellipsoids are drawn at the 40% probability level.

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Structure Determination of Bromotricarbonyl(η-cyclopentadienyl)molybdenum(II)

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Abstract. [$(\eta\text{-}C_5H_5)Mo(CO)_3Br$], $M_r = 324·97$, monoclinic, $P2_1/n$, $a = 8·186\ (3)$, $b = 10·536\ (3)$, $c = 11·391\ (3)$ Å, $\beta = 99·58\ (2)°$, $V = 968·7\ (6)$ Å^3, $Z = 4$, $D_x = 2·228$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 56·68$ cm^{-1}, $F(000) = 616$, $T = 113\ (1)$ K, final $R = 0·0261$ for all 1271 independent reflections. The molecule adopts a distorted square pyramidal coordination environment about the Mo atom. The shorter Mo—C bond of the carbonyl ligand *trans* to the bromide apparently arises from the lack of competition for $d\pi$ bonding electrons. The longer Mo—C bonds for the mutually *trans* carbonyl ligands, and the squashed *trans* C—Mo—C angle (approximately 28° smaller than the Br—Mo—C_{trans} angle) result from sharing one pair of $d\pi$ bonding electrons. Selected bond distances and angles: Mo—Br = 2·651 (1), av. Mo—C_{cis} = 2·020 (6), Mo—C_{trans} = 1·978 (7), Mo—CP_{cent} = 1·993 (1), av. $(C—O)_{cis}$ = 1·132 (5), $(C—O)_{trans}$ = 1·154 (9), Br—Mo—C_{trans} = 136·7 (2), Br—Mo—C_{cis} = 77·0 (3), Br—Mo—CP_{cent} = 112·04 (3), av. C_{trans}—Mo—C_{cis} = 78·1 (2), av. C_{cis}—Mo—CP_{cent} = 125·8 (2), C_{trans}—Mo—CP_{cent} = 111·3 (2).

Experimental. Bromotricarbonyl(η-cyclopentadienyl)molybdenum(II) was isolated as a byproduct from the bromination of bis[(η-cyclopentadienyl)-dicarbonylmolybdenum(II)]. Red-brown crystals were grown from cold toluene (250 K).

A crystal of dimensions 0·3 × 0·3 × 0·1 mm was mounted in air on a glass fiber. Lattice parameters were determined by a least-squares fitting of 15 reflections ($15 < 2\theta < 30°$). Experiments were carried out on a Syntex $P2_1$ diffractometer equipped with an LT-1 low-temperature system under the following conditions: graphite-monochromated Mo $K\bar{\alpha}$ radiation, θ–2θ scan mode, scan speed 1·0 to 20° min^{-1}, scan width (1·2° + dispersion), background one-sixth of the total scan at both edges, $4·0 < 2\theta < 45°$; 1534 reflections were measured, 1271 unique ($R_{int} = 0·028$) reflections were obtained, systematic absences were found at $k = 2n + 1$ in $0k0$, $l = 2n + 1$ in $h0l$. I_o

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$< 0{\cdot}2\sigma_{I_o}$ were reset to $I_o = 0{\cdot}2\sigma_{I_o}$. The index range was $-8 \le h \le 8, 0 \le k \le 11, -12 \le l \le 0$. Two reflections were monitored after every 100 measurements; crystal decay during data collection ≤ 2%. Empirical absorption corrections were applied (± 40·3%). The maximum correction of the extinction parameters is 0·571 for the 020 reflection. The structure was solved by the heavy-atom method.

Non-H atoms were refined with anisotropic thermal parameters by a full-matrix least-squares method. All H atoms were located in the difference electron density map, and the positional parameters and isotropic thermal parameters were refined. The function $\sum w(|F_o| - k|F_c|)^2$ was minimized with $w = 1/\sigma(F_o)^2$. 139 variables. Final $R = 0{\cdot}0261$, $wR = 0{\cdot}0372$, $S = 1{\cdot}0377$, Δ/σ (av.) = 0·144, Δ/σ (max.) = 2·06 [y coordinate of H(5)]. The largest peak found in the final difference Fourier map was $+0{\cdot}37\ \text{e}\ \text{Å}^{-3}$ at 1·16 Å from the Mo atom, while the largest negative peak was $-0{\cdot}11\ \text{e}\ \text{Å}^{-3}$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a VAX 8600 computer using the *KUDNA* system (Takusagawa, 1984). An atom-numbering scheme for the title compound is shown in Fig. 1. Atomic coordinates and selected bond distances and angles are collected in Tables 1 and 2, respectively.*

Related literature. Structural studies of related piano stool complexes: Chaiwasie & Fenn (1968), Mawby & Pringle (1972) and Bueno & Churchill (1981). Studies relevant to the preparation and reactivity of (η-C_5H_5)Mo(CO)$_3X$ complexes: Curtis, Fotinos, Han & Butler (1983) and Starker & Curtis (1985).

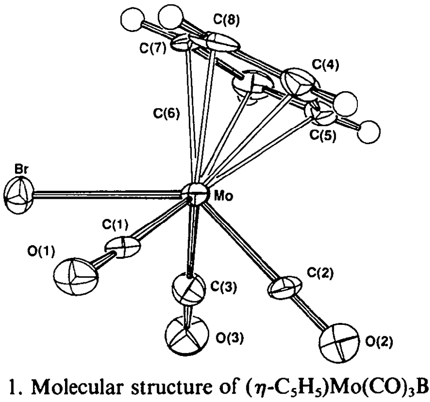

Fig. 1. Molecular structure of (η-C_5H_5)Mo(CO)$_3$Br.

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for* $C_8H_5BrMoO_3$

	x	y	z	B_{eq}*
Mo	0·86177 (4)	0·29200 (4)	0·64212 (4)	1·19
Br	0·89316 (6)	0·25934 (5)	0·87558 (6)	1·95
C(1)	0·6263 (7)	0·3058 (4)	0·6744 (6)	1·60
O(1)	0·4950 (5)	0·3089 (3)	0·6932 (4)	2·11
C(2)	0·7674 (6)	0·4222 (4)	0·5251 (5)	1·63
O(2)	0·7143 (4)	0·4983 (4)	0·4563 (4)	2·83
C(3)	0·9864 (6)	0·4490 (5)	0·7056 (6)	2·12
O(3)	1·0632 (5)	0·5345 (4)	0·7410 (5)	3·06
C(4)	0·8415 (6)	0·1590 (5)	0·4812 (6)	2·52
C(5)	0·9978 (7)	0·2226 (5)	0·4950 (6)	1·87
C(6)	1·0945 (7)	0·1805 (5)	0·6017 (6)	2·19
C(7)	0·9996 (7)	0·0921 (5)	0·6551 (6)	2·32
C(8)	0·8443 (7)	0·0808 (5)	0·5808 (6)	2·61

$*B_{eq} = \frac{8}{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j.$

Table 2. *Selected bond distances* (Å) *and angles* (°) *for* $C_8H_5BrMoO_3$

Mo—Br	2·651 (1)	Mo—CP*	1·993 (1)
Mo—C(1)	2·027 (4)	C(1)—O(1)	1·131 (5)
Mo—C(2)	1·978 (7)	C(2)—O(2)	1·154 (9)
Mo—C(3)	2·014 (6)	C(3)—O(3)	1·133 (8)
Mo—C(4)	2·291 (8)	C(4)—C(5)	1·430 (7)
Mo—C(5)	2·281 (7)	C(4)—C(8)	1·399 (12)
Mo—C(6)	2·348 (4)	C(5)—C(6)	1·406 (13)
Mo—C(7)	2·382 (5)	C(6)—C(7)	1·414 (7)
Mo—C(8)	2·330 (6)	C(7)—C(8)	1·410 (11)
Br—Mo—C(1)	76·3 (3)	C(1)—Mo—CP*	126·0 (2)
Br—Mo—C(2)	136·7 (2)	C(2)—Mo—CP*	111·3 (2)
Br—Mo—C(3)	77·7 (2)	C(3)—Mo—CP*	125·6 (1)
Br—Mo—CP	112·04 (3)	Mo—C(1)—O(1)	177·5 (4)
C(1)—Mo—C(2)	78·2 (2)	Mo—C(2)—O(2)	179·1 (2)
C(1)—Mo—C(3)	108·4 (2)	Mo—C(3)—O(3)	176·8 (3)
C(2)—Mo—C(3)	77·9 (3)		

* CP = calculated centroid of the CP ring.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates, and a complete list of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52535 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.